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Properties of Functionalized Silica-Reinforced Fluoropolymers

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Introduction

The properties of the fluorine atom coupled with its covalent bond strength with carbon facilitates the synthesis of compounds that possess unique properties. High molecular weight fluorinated polymers, for instance, are chemically inert, thermally stable, often possess very low dielectric constants and dissipation factors, demonstrate very low surface friction, and are intrinsically flame retardant. They also exhibit some disadvantages including marginal abrasion resistance, poor machining properties, low tensile strength and modulus, and propensity to creep under mechanically loaded conditions, restricting use in some applications. Particulate reinforcement in fluoropolymer hosts has been demonstrated to improve some of these shortcomings. For instance, high aspect ratio glass and carbon fibers have been incorporated into polytetrafluoroethylene (PTFE) promoting enhancements in yield strength, break strength, modulus, and creep.^{1,2} Ceramic nanoparticles have been shown to provide abrasion resistance to PTFE as well.³ The achievement of these enhancements is largely predicated on requisite adhesion between the host and reinforcing agent, often posing a formidable challenge due to the electronic nature of fluorinated polymers.⁴ To date, studies on the augmentation of the mechanical and wear properties of fluoropolymers have been nearly exclusive to PTFE rather than its more processable, partially fluorinated derivatives such as fluorinated ethylene propylene (FEP), perfluoroalkoxy (PFA), polychlorotrifluoroethylene (PCTFE), and polyvinylidene fluoride (PVDF).

Recently, our group reported a method to produce fluoroalkyl-functionalized silica particles of nanoscale dimensions.⁵ The aim of this work is to investigate the properties afforded by integration of these particles into FEP in comparison with composites similarly fabricated from commercial grades of nanosilica, with the expectation that fluoroalkyl functionalization will facilitate superior particulate dispersion.

Experimental

Materials. FEP 100 was purchased from DuPont. Aerosil 380, 7 nm diameter fumed silica, 390 (40 m²/g surface area) was purchased from Evonik Degussa Corporation. Fluorinated silane reagents (heptadecafluoro-1,1,2,2-tetrahydrodecyl) dimethylchlorosilane (fluorodecyl monochlorosilane or FDec-MCS); (tridecafluoro-1,1,2,2-tetrahydrodecyl)dimethylchlorosilane (FOct-MCS); (3,3,3-trifluoropropyl)dimethylchlorosilane (FPro-MCS); (heptadecafluoro-1,1,2,2-tetrahydrodecyl)methylchlorosilane (fluorodecyl dichlorosilane or FDec-DCS); and (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trichlorosilane (fluorodecyl trichlorosilanes or FDec-TCS) were purchased from Gelest, Inc. 1,3-Dichloro-1,2,2,3,3-pentafluoropropane (AK-225G) was purchased from AGC Chemicals Americas, Inc. Anhydrous dimethylamine was purchased from Aldrich. The preceding materials were all used as received from the manufacturer. Reagent grade chloroform was purchased from Aldrich and passed through an activated alumina column prior to use.

Fluoroalkyl Functionalization of Silica Particles. The surface functionalization of silica particles was performed using Schlenk line techniques, taking great care to minimize moisture exposure. Silica particles (2 g), in a 250 mL roundbottom flask, were initially dried by heating overnight at 200°C under dynamic vacuum. The dried silica was allowed to cool to room temperature under vacuum and then stirred under 1 atm of dimethylamine for 17 h. The silica particles were then suspended in 80 mL of dry chloroform. A 4-fold excess of fluoroalkyl-substituted chlorosilane reagent (e.g., 7.00 g FDec-MCS), assuming a maximum grafting density of 4 $\mu\text{mol}/\text{m}^2$,^{38,45,48} was then added via syringe. The reaction mixture was allowed to stir for 3 days in a dry nitrogen environment before the fluoroalkyl-functionalized silica particles were recovered by centrifuge and purified by exhaustive Soxhlet extraction in chloroform. The extraction was allowed to

proceed for 3 days in a nitrogen environment to ensure the removal of any noncovalently bound chlorosilane-derived species or other surface contaminants. After the extraction process, the particles were dried in a stream of nitrogen, transferred to vials, and dried at 100°C under dynamic vacuum for approximately 1 h. A typical yield was 2.0–2.5 g of modified silica.

Composite Fabrication. Polymer blending with nanosilica was performed using a 5 cm³ capacity DSM Xplore twin screw batch micro-compounding machine. All mixing was performed at 310°C for 3 minutes under a continuous nitrogen purge. After mixing, the extrudate was used in injection molding operations to produce 1 inch diameter, 1/16 in. thick disks for rheological investigation. Thin slices of the extrudates were melt pressed between glass slides at 310°C under vacuum for optical microscopy.

Rheology. Variable frequency complex oscillatory isothermal rheometry on polymer melts was conducted on an Anton Paar MCR 500 instrument in parallel plate configuration (gap width = 1.0 mm) above the equilibrium melting temperature of FEP 100 (330°C) at a strain of 0.1% within the linearly viscoelastic regime of the fluoropolymer. The investigated frequency range was between 0.05 and 500 s⁻¹.

Results and Discussion

Rheological investigation of FEP 100 and nanosilica-containing composites was conducted in oscillatory shear at variable frequency at 330°C, the results of which are depicted in Figure 1. The complex viscosity of the neat fluoropolymer is relatively insensitive to frequency up to 10 s⁻¹ where it experiences shear thinning due to rapid polymer chain alignment and disentanglement with the shear field. Incorporation of 2.5, 5, and 10 wt.% Aerosil 380 results in increasing viscosity, especially in the latter two compositions where a one and two order of magnitude increase in viscosity was measured, respectively. Shear thinning for the 5% and 10% Aerosil 380 composites occurs immediately during the experiments, indicating disruption of an aggregated silica network structure consistent with poor particle miscibility in the fluoropolymer host. On the other hand, composites fabricated from F-Dec functionalized silica demonstrate reduced viscosity in relation to the neat polymer, with the exception of the composition containing 10 wt.% silica which shows quantitatively similar behavior to the 5 wt.% Aerosil 380 blend. This contrast in behavior suggests good dispersion of the F-Dec silica in the FEP 100, therefore acting as a plasticizer by reducing chain entanglements and interactions.

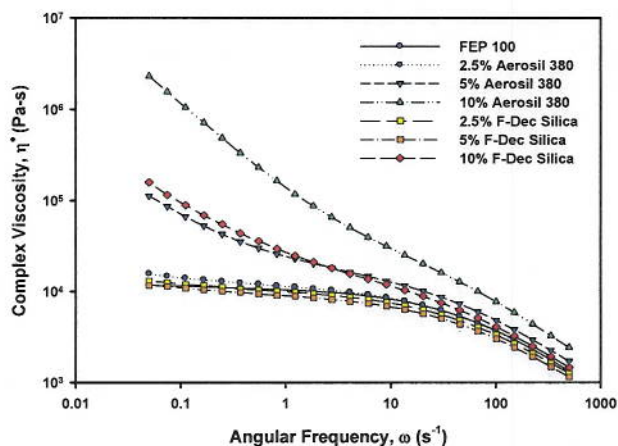


Figure 1. Plots of complex viscosity vs. angular frequency for FEP 100 and nanosilica-containing composites.

Examination of the morphologies of the subject composites by transmission optical microscopy confirms rheological observations as shown in Figure 2. As expected, no network structure is witnessed in the pure FEP micrograph. The composite containing 5 wt.% Aerosil 380 shows poor miscibility and a phase separated silica network whereas the blend containing 5% F-Dec functionalized silica exhibits no phase separation at the visible light scattering length scale. Also corroborating rheological evidence, Figure 3

depicts a phase separated network of silica nanoparticles in the 10 wt.% containing F-Dec functionalized silica composite.



Figure 2. Transmission optical micrographs of A) FEP 100, B) FEP 100 & 5 wt.% Aerosil 380, and C) FEP 100 & 5 wt.% F-Dec Silica. The scalebar denotes 20 microns.

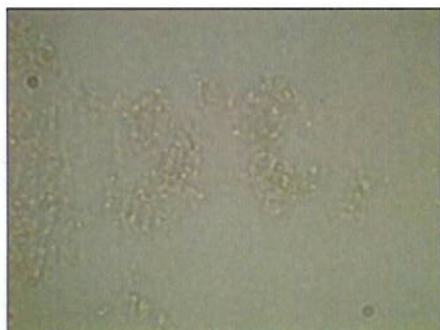


Figure 3. Transmission optical micrograph of FEP 100 and 10 wt.% F-Dec Silica at equivalent magnification as in Figure 2.

Conclusions

F-Dec functionalized silica has demonstrated good compatibility with FEP 100 at concentrations equivalent to or less than 5 weight percent as evidenced by variable frequency parallel plate rheometry experiments confirmed by transmission optical microscopy. Mechanical reinforcement of fluoropolymers in the solid state containing a good dispersion of silica is currently being investigated, as well as any effects on polymer crystallization behavior. The poor dispersion of Aerosil 380 in FEP 100 is likely due to surface silanol groups which have a higher affinity for each other through hydrogen bonding over interactions with the host fluoropolymer.

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